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Oxygen Plasma Followed by High-Pressure H_2O Vapor Heat Treatment Used for Passivation of Silicon Surfaces

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Abstract. We report passivation of silicon surfaces by combination of oxygen plasma with high-pressure H_2O vapor heat treatment. 150 μm-thick n-type silicon substrates were treated with radio frequency (RF) oxygen plasma at 100 W, 133 Pa and room temperature for 1 min. The samples were subsequently heated with $8x10^5$ Pa H_2O vapor at 240°C. 3.5 nm thick SiO_2 layers were formed on the surfaces. The effective minority carrier lifetime and recombination velocity were estimated to be 440 μs and 17 cm/s. Those results indicate a possibility of passivation of silicon surfaces with thin SiO_2 layers at 240°C.

Introduction

We want to passivate silicon surfaces well by forming thin oxide layers, which allow tunneling effect current in order to fabricate solar cells [1]. When silicon passivated with thin oxide layers is sandwiched by two different kinds of metals, the difference in their work functions can cause built in potential in silicon. Holes and electrons excited by light illumination in silicon are separated each other. Holes move to the metal with a high work function according to the internal built in potential distribution. On the other hand, electrons move to the metal with a low work function. Photo induced current are consequently produced through tunneling current via thin oxide layers.

In this paper, we discuss combination of oxygen plasma treatment with high-pressure H_2O vapor heat treatment to achieve passivation of silicon surfaces by forming thin oxide layers on silicon surfaces at low temperature [2,3]. We report analyses of the effective minority carrier lifetime, recombination velocity, and oxide thickness to discuss passivation of silicon surface at low temperatures.

Experimental procedure

150-μm thick n-type silicon wafers were prepared. Native oxide was removed by 5% diluted HF solution. Top surfaces of the silicon substrates were then irradiated with 100-W RF plasma at an oxygen gas pressure of 133 Pa and room temperature for 1 and 3 min. The other rear surfaces of the silicon substrates were subsequently irradiated with oxygen plasma in the same manner. Some substrates were kept with no plasma treatment for making high pressure H_2O vapor heat treatment alone. The samples were then annealed with $8x10^5$-Pa H_2O vapor at temperature ranging from 220 to 260°C for 3 h. The minority carrier effective lifetime τ_{eff} was

precisely analyzed by the photo-induced carrier microwave absorption method, as shown by a schematic apparatus in Fig. 1 [4,5]. The 9.35 GHz microwave transmittance measurement system was constructed using waveguide tubes. It had a narrow gap for placing a sample wafer. A small hole was opened on a wall of the waveguide to place an optical fiber for introducing light from a 620 nm light-emitting diode (LED). The light was switched by switching the operation voltage applied to the diode with pulse widths ranging from $1x10^{-5}$ to $1x10^{-2}$ s. A Teflon plate was placed aslant in the waveguide tube to reflect and diffuse LED light. Consequently, the sample was uniformly illuminated at 1.55 mW/cm^2 with LED light pulses. Microwave was coincidentally switched with the light pulse turned ON or OFF, respectively, using a coincident switching circuit to obtain changes in microwave transmittance during light ON or OFF. The microwave, which transmitted the sample, was rectified using a high-speed diode and integrated with time with a time constant of 5 s. The integrated voltages with different pulse widths was analyzed to determine τ_{eff}. In the case of τ_{eff} lower than $1x10^{-5}$ s, continuous wave (CW) light illumination was used. τ_{eff} was obtained as,

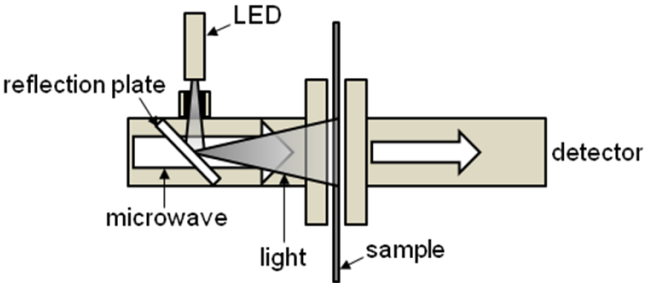

Fig. 1: Schematic apparatus of microwave transmittance measurement system.

$$\tau_{eff} = \frac{N}{G} \quad , \tag{1}$$

where N is photo induced minority carrier density per unit area and G is a carrier generation rate of $2.81x10^{15}$ s^{-1}cm^{-2}, which was previously determined by comparison of periodically pulsed light illumination measurement with CW light illumination measurement [5]. The recombination velocity of silicon surfaces S was estimated from the minority carrier lifetime. We supposed that the bulk lifetime was long enough, and that τ_{eff} was governed by S. S was given as,

$$S = \frac{d}{2\tau_{eff}} \quad , \tag{2}$$

where d is the thickness of silicon wafer [6,7].

SiO_2 formation and its thickness were investigated by analysis of optical reflectivity spectra. Silicon wafer coated with 12.6 nm-thick thermally grown SiO_2 layers was used as a reference. Reflectivity spectra of samples $R(\lambda)$, where λ is wavelength, and the reference $R_r(\lambda)$ were measured in ultraviolet range between 250 and 340 nm. The ratio of $R(\lambda)/R_r(\lambda)$ was precisely analyzed by numerical calculation program constructed with the multiple layered Fresnel coefficient model and refractive indexes of SiO_2 and crystalline silicon which depended on wavelength [8]. Fitting calculated $R(\lambda)/R_r(\lambda)$ to experimental $R(\lambda)/R_r(\lambda)$ gave the optical judge of SiO_2 formation and its thickness.

Results and discussion

τ_{eff} of initial bare silicon wafers was 4.6 μs in average. Oxygen plasma treatment for 1 and 3 min. decreased τ_{eff} to 0.9 and 1.6 μs, respectively, as shown by an arrow A on the vertical axis in Fig. 2. Those τ_{eff} resulted in that oxygen plasma treatment increased *S* to 8550 and 4350 cm/s, respectively, as shown by arrows on the vertical axis in Fig. 3. $8x10^5$ Pa H_2O vapor heat treatment for 3 h increased τ_{eff}, as shown in Fig. 2. In the case of oxygen plasma treatment for 3 min, τ_{eff} increased to 210 μs as temperature of H_2O vapor heating increased to 240°C and it almost leveled off for H_2O vapor heating above 240°C. On the other hand, τ_{eff} markedly increased to 440 μs as temperature of H_2O vapor heating increased to 240°C in the case of oxygen plasma treatment for 1 min. It decreased to 240 μs as temperature of H_2O vapor heating further increased to 260°C. In contrast, τ_{eff}, was low on the order of 10 μs when $8x10^5$ Pa H_2O vapor heat treatment alone was applied. Those results of Fig. 2 show that oxygen plasma had an important role for silicon surface passivation. We believe that oxygen plasma incorporated oxygen atoms into the silicon surface regions, although it alone did not complete surface passivation. High pressure H_2O vapor heat treatment clearly passivated the silicon surfaces. Our previous study has revealed that high pressure H_2O vapor heat treatment makes Si-O bonding networks stable [2]. We believe that thin and stable SiO_2 layers were formed on the silicon surfaces by bonding silicon and oxygen atoms incorporated by oxygen plasma during $8x10^5$ Pa H_2O vapor heat treatment at 240°C for 3 h. It is interesting that oxygen plasma only for 1 min. was effective for surface passivation with high τ_{eff}. It suggests a possibility of surface passivation by formation of thin SiO_2 layer on the silicon surfaces. *S* markedly decreased to 17 and 35 cm/s for oxygen plasma treatment for 1 and 3 min, respectively, followed by $8x10^5$ Pa H_2O vapor heat treatment at 240°C for 3 h, as shown in Fig. 3. The very low recombination probability of hole minority carriers was achieved by the low temperature processes.

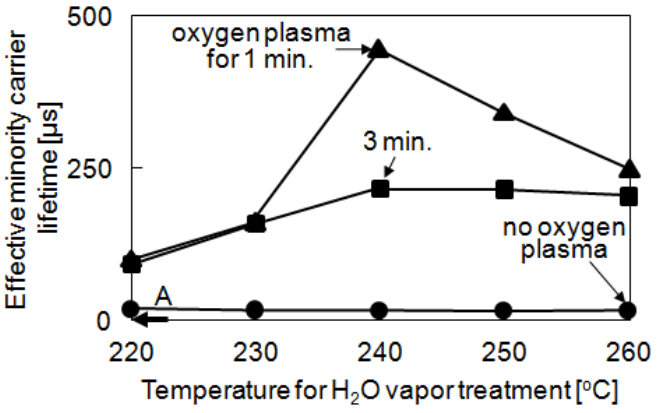

Fig. 2: Effective minority carrier lifetime of n-type silicon wafers as a function of temperature for $8x10^5$ Pa H_2O vapor heat treatment for 3 h. The arrow *A* presents lifetime as-oxygen plasma treated for 1 and 3 min.

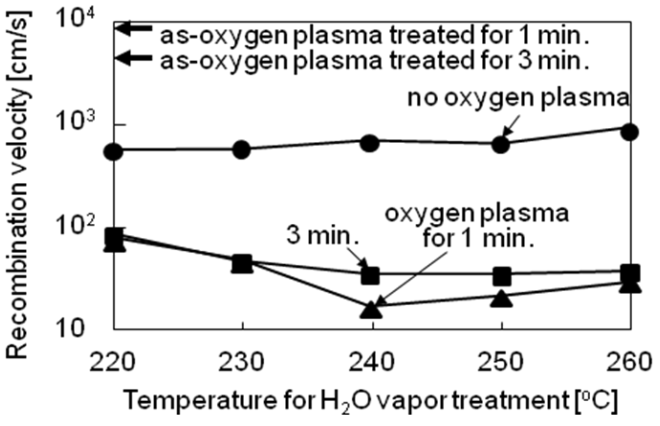

Fig. 3: Recombination velocity of n-type silicon wafers as a function of temperature for $8x10^5$ Pa H_2O vapor heat treatment for 3 h.

Figure 4 shows experimental and calculated normalized reflectivity ratio. The ratio of $R(\lambda)/R_r(\lambda)$ defined in Experimental procedure was normalized by that at 250 nm $R(250)/R_r(250)$. An experimental spectrum was presented for oxygen plasma treatment for 1 min. followed by $8x10^5$ Pa H_2O vapor heat treatment at 240°C for 3 h in Fig. 4. Calculated spectra were also

presented for the SiO_2 thickness ranging from 0 to 4 nm with a 0.5 nm step. The normalized reflectivity ratio increased as the SiO_2 thickness increased for every wavelength because the reflectivity ratio increases 1 as the SiO_2 thickness increased 12.6 nm. Anti-reflection effect is high in low wave length region because of high refractive index of SiO_2 in low wave length region. This effect resulted in low normalized reflectivity ratio for long wavelength region, as shown in Fig. 4. There was a good coincidence between the experimental spectrum and the calculated spectrum with 3.5-nm thick SiO_2 layer.

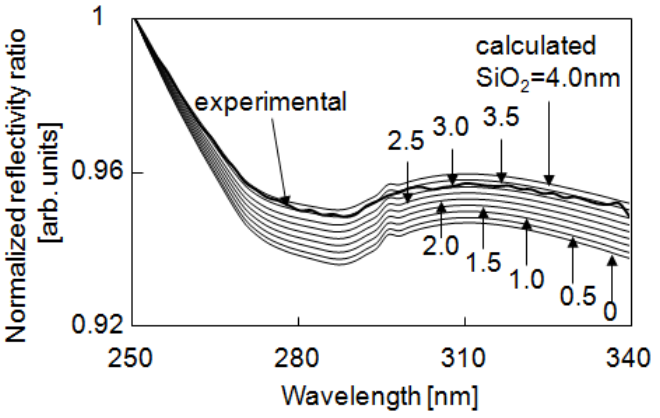

Fig. 4: Experimental and calculated normalized reflectivity ratio. The ratio of $R(\lambda)/R_r(\lambda)$ defined in Experimental procedure was normalized by that at 250 nm $R(250)/R_r(250)$.

Figure 5 shows the thickness of SiO_2 layer analyzed by the method described above as a function of temperature of $8x10^5$ Pa H_2O vapor heat treatment for 3 h. Similar values of the SiO_2 thickness were obtained among temperatures of H_2O vapor heating between 220 and 260°C for each oxygen plasma condition. The thickness of SiO_2 layer was estimated to be 3.5 nm in average for oxygen plasma treatment for 1 min, which was lower than 4.5 nm in average formed by oxygen plasma for 3 min. The long τ_{eff} of 440 μs was achieved by formation of 3.5-nm thick SiO_2 layer of the silicon surfaces. On the other hand, 2-nm thick SiO_2 layer was also formed when bear silicon was heated with $8x10^5$ Pa H_2O vapor for 3 h alone. Optimum conditions of oxygen plasma and H_2O vapor heat treatment should be further investigated to achieve passivation by formation of SiO_2 layers thinner than 2 nm.

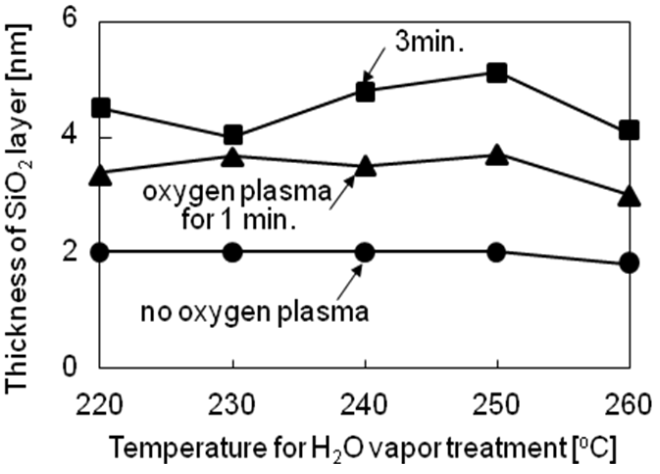

Fig. 5: Thickness of SiO_2 layer as a function of temperature for $8x10^5$ Pa H_2O vapor heat treatment for 3 h.

Summary

The passivation of the silicon surfaces was investigated using combination of oxygen plasma treatment with high pressure H_2O vapor heat treatment. 150-μm thick n-type silicon substrates were irradiated with 100-W RF plasma at an oxygen gas pressure of 133 Pa and room temperature for 1 and 3 min. Samples were subsequently annealed in $8x10^5$ Pa H_2O vapor from 220 to 260°C for 3 h. τ_{eff} was obtained by analysis of the photo-induced carrier microwave absorption. The thickness of SiO_2 layer was estimated by analysis of optical reflectivity spectra.

τ_{eff} increased to 440 μs as temperature of H_2O vapor heating increased to 240°C for oxygen plasma treatment for 1 min, while it increased to 210 μs at most for oxygen plasma treatment for 3 min. *S* was estimated to be 17 and 35 cm/s for oxygen plasma treatment for 1 and 3 min, respectively. Formation of SiO_2 layer on the silicon surfaces was observed. The thickness of SiO_2 layer was estimated to be 3.5 and 4.5 nm for oxygen plasma treatment for 1 and 3 min, respectively. These results indicate a possibility of effective passivation of silicon surfaces by combination of oxygen plasma treatment with high pressure H_2O vapor heat treatment at 240°C.

Acknowledgments

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